

SHORT COMMUNICATION

Asymmetric-Selective Polymerization of 2,3-Epoxypropyl Methacrylate with Grignard Reagent-(–)-Sparteine Systems in Toluene at –78°C

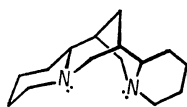
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(Received November 30, 1977)

KEY WORDS Asymmetric-Selective Polymerization / Stereoelective Polymerization / Grignard Reagent / (–)-Sparteine / 2, 3-Epoxypropyl Methacrylate / Poly(2, 3-epoxypropyl methacrylate) /

We have recently reported on the highly asymmetric-selective (or stereoelective) polymerization of (*RS*)- α -methylbenzyl methacrylate [(*RS*)-MBMA] using Grignard reagent-(–)-sparteine systems as asymmetric catalysts in toluene.¹ In



(–)-Sparteine

this polymerization, an (*S*)-polymer was formed initially, whose optical purity was about 90%, and the optical purity of unreacted (*R*)-monomer was greater than 90% with about a 60-% polymer yield. It is therefore of interest to see whether or not this catalyst system can polymerize stereoelectively a methacrylic ester which has an asymmetric center at a further remote δ -position from the carbon—carbon double bond. As such a monomer, which is commercially available, 2, 3-epoxypropyl (glycidyl) methacrylate (EPMA) was polymerized with cyclohexylmagnesium bromide (c-HexMgBr)- or chloride (c-HexMgCl)-(–)-sparteine system in toluene at –78°C. The asymmetric-selective polymerization proceeded to form a highly isotactic polymer which had not been obtained with typical anionic catalysts such as butyllithium and Grignard reagents.²

The polymerization of EPMA was carried out in the same manner as described in a previous

paper.¹ The polymer was first precipitated in diethyl ether and purified by reprecipitation from a chloroform solution into methanol; unreacted EPMA was recovered by distillation from the ether solution. The optical rotations (unit: deg cm²/10 g) of the polymer (*c*, about 2 g/dl in chloroform) and the recovered monomer (neat) were measured with a 5-cm cell and 0.5—2-cm cells, respectively, on a Yanagimoto Direct Reading Polarimeter OR-10; the precision of reading was $\pm 0.003^\circ$. The ¹H NMR spectrum of the polymer was taken with a JEOL-MH-100 (100 MHz) spectrometer in CDCl₃ at 60°C. Optically active 2, 3-epoxypropanol ($[\alpha]_D^{25} - 0.26^\circ$, neat, 10 cm) was obtained by the hydrolysis of the recovered monomer ($[\alpha]_D^{25} - 0.60^\circ$, neat, 10 cm) with sodium hydroxide in water at 0°C. From the above results and the $[\alpha]_D^{25} + 15^\circ$ (neat) reported for optically pure (*R*)-2, 3-epoxypropanol,³ the $[\alpha]_D^{20}$ of the optically pure (*S*)-EPMA was estimated to be -35° .

The results of the polymerization are summarized in Table I. Both the c-HexMgBr and c-HexMgCl systems polymerized preferentially (*R*)-EPMA over (*S*)-EPMA, and showed little difference. The optical purity (α_p) of the polymer was calculated using the relationship, $\alpha_p \times Y_p = \alpha_m \times (100 - Y_p)$, where α_m is the optical purity of the unreacted monomer, and Y_p is the polymer yield (%). This relationship was satisfied in the polymerization of (*RS*)-MBMA by the same catalyst systems.¹ Using the $[\alpha]_D^{20}$ of the polymer

Table I. Polymerization of EPMA with the *c*-HexMgBr- or *c*-HexMgCl(-)-sparteine system in toluene at $-78^{\circ}\text{C}^{\text{a}}$

<i>c</i> -HexMgX	EPMA		Yield, %	$\eta_{\text{sp}}/c^{\text{b}}$, dl/g	$[\alpha]_{\text{D}}^{20}([\alpha]_{427}^{20})$ of polymer, deg	$\alpha_{\text{p}}^{\text{c}}$, %	$[\alpha]_{\text{D}}^{20}(\alpha_{\text{m}})$ of ^d unreacted monomer, deg
	Toluene, g/ml	Time, hr					
Br	1.5/15	26	23	0.23	+4.1 (+8.4)	16	-1.67 (4.8)
Br	1.5/15	45	7	0.29	+3.6 (+7.7)	16	-0.41 (1.2)
Br	4/20	49	10	0.36	+4.7 (+8.9)	23	-0.88 (2.5)
Br	5/20	45	15	0.37	+3.6 (+7.4)	16	-0.99 (2.9)
Br	10/40	45	21	0.28	+3.6 (+7.2)	18	-1.65 (4.8)
Cl	1.5/15	49	18	0.25	+4.1 (+7.9)	21	-1.56 (4.5)

^a [*c*-HexMgX]/[(-)-sparteine]=1/1.2; [EPMA]/[*c*-HexMgX]=20/1.

^b Chloroform solution at 30.0°C , $c=0.5$ g/dl.

^c Optical purity of polymer calculated from polymer yield and optical purity of unreacted monomer.

^d The $[\alpha]_{427}^{20}$ values were slightly less than the double of corresponding $[\alpha]_{\text{D}}^{20}$. The values in parentheses are optical purity (%) calculated on the basis of $[\alpha]_{\text{D}}^{20}-35^{\circ}$ for optically pure (*S*)-EPMA.

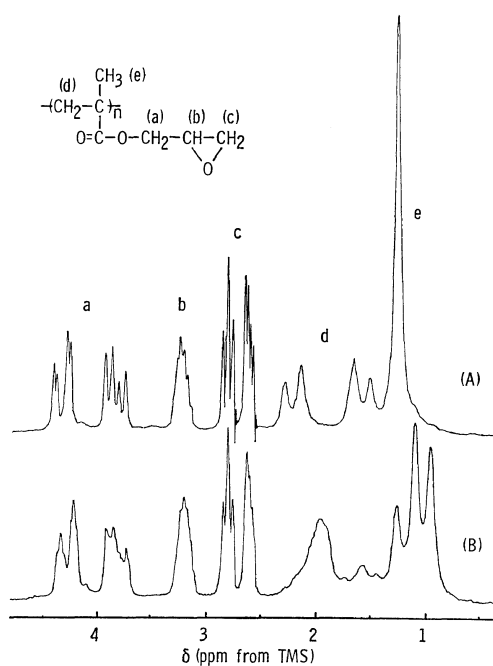


Figure 1. ^1H NMR spectra of poly(EPMA) obtained by the *c*-HexMgBr(-)-sparteine (1/1.2) system (A) and *c*-HexMgBr alone (B) in toluene at -78°C .

and α_{p} values in Table I, the $[\alpha]_{\text{D}}^{20}$ of optically pure poly [(*R*)-EPMA] was calculated to be $+22 \pm 3^{\circ}$. The correlation between $[\alpha]_{\text{D}}^{20}$ and α_{p} values was scattered. This may be ascribed to the small observed optical rotation and the uncertainty of the polymer yield due to the presence of a small

amount of oligomeric products soluble in methanol. The asymmetric selectivity of the catalyst against (*RS*)-EPMA was lower compared with the selectivity against (*RS*)-MBMA,¹ but seems to be comparable to the selectivity reported in the ring-opening polymerization of propylene oxide which contains an analogous asymmetric carbon.^{4,5}

In Figure 1 are shown the ^1H NMR spectra of the polymers which were obtained with *c*-HexMgBr(-)-sparteine (1/1.2) system and with *c*-HexMgBr alone in toluene at -78°C . The triad tacticity of the polymers was determined directly from the spectra.^{2,6} The optically active polymer was nearly 100% isotactic, while the polymer obtained with *c*-HexMgBr alone was atactic. It has been reported that the isotacticity of poly(EPMA) obtained with butyllithium and Grignard reagents in toluene at -78°C was about 30% and only lithium aluminum hydride yielded an isotactic (about 80%) polymer.² The Grignard reagent(-)-sparteine system may be the first catalyst to give poly(EPMA) of nearly 100% isotacticity. Judging from the ^1H NMR spectra, almost all epoxy groups remained unreacted during the polymerization.

The present Grignard reagent(-)-sparteine systems were unique and interesting catalysts in the polymerization of EPMA from the viewpoint of not only its asymmetric selectivity but also its stereospecificity. The highly isotactic polymer may be useful as a polymer reagent because it has a highly ordered tactic chain and reactive epoxy groups in addition to the asymmetric character.

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REFERENCES

1. Y. Okamoto, K. Ohta, and H. Yuki, *Chem. Lett.*, 617 (1977).
2. Y. Iwakura, F. Toda, T. Ito, and K. Aoshima, *J. Polym. Sci., Part B*, **5**, 29 (1967).
3. J. C. Sowden and H. O. L. Fischer, *J. Am. Chem. Soc.*, **64**, 1291 (1942).
4. S. Inoue, T. Tsuruta, and N. Yoshida, *Makromol. Chem.*, **79**, 34 (1964).
5. C. Coulon, Spassky, and P. Sigwalt, *Polymer*, **17**, 821 (1976).
6. Y. Iwakura, F. Toda, T. Ito, and K. Aoshima, *Makromol. Chem.*, **104**, 26 (1967).